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Mechanistic studies of CO_2 reduction to methanol mediated by an N-heterocyclic germylene hydride†

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The labile germylene hydride $L^{Cy}GeH$ is capable of activating CO_2 affording the corresponding formate $L^{Cy}GeOCH(=O)$ (**2**) (L^{Cy} = cyclo-C_6H_8-1-NAr-2-C(Ph)NAr, Ar = 2,6-$iPr_2C_6H_3$). Compound **2** and the previously reported LGeOCH(=O) (L = CH(MeC=NAr)$_2$, Ar = 2,6-$iPr_2C_6H_3$) (**2′**) could be further converted to methanol with the $AlH_3{\cdot}NMe_3$ alane-amine adduct as a hydrogen source upon workup with water. A plausible mechanism for the conversion of the formate complexes to methanol is proposed based on additional results from the conversion of **2′** with the milder hydride delivery agent $LAlH_2$.

Introduction

The activation and conversion of carbon dioxide to valuable chemicals are attracting increasing attention in chemical research due to the energy and climate crisis.[1] Hydrogenation of carbon dioxide to other C1 feedstocks, such as formic acid, methanol and methane, is one of the most straightforward approaches for utilising CO_2.[2] The process, which is catalysed by transition metal complexes, has been significantly developed in the last decade.[2,3] Small molecule activation represents one of the most crucial research topics in contemporary main group chemistry.[4] However, examples of CO_2 hydrogenation mediated by main-group pre-catalysts are still scarce. Recently, N-heterocyclic carbenes (NHCs) demonstrated by Ying *et al.*[5] and 'Frustrated Lewis Pair' (FLP) systems reported by Stephan[6] and Piers[7] were shown to serve as suitable hydrogenation systems. In line with that, Roesky *et al.* have demonstrated that the germylene hydride LGeH (L = CH(MeC=NAr)$_2$, Ar = 2,6-$iPr_2C_6H_3$) can activate CO_2 affording a germylene formate complex LGeOCH(=O) (**2′**),[8] which can be further converted to formic acid and methanol upon hydrolysis with water using $LiNH_2{\cdot}BH_3$ and $NH_3{\cdot}BH_3$ adducts as hydride sources.[9] In addition, they proposed a possible mechanism for the latter case based on NMR spectroscopic investigations, but no intermediates were isolated in this study. Very recently, a theoretical study by Sakaki *et al.* has shown that LGeH could also act as a catalyst for CO_2 hydrosilylation to $F_3SiOCH(=O)$ when $HSiF_3$ is used as the hydride source.[10] Until now, there have been only two examples of using the germylene hydride complexes bearing β-diketiminato ligands for CO_2 activation,[11] so it seems desirable to apply varied ligand scaffolds to stabilise the highly active germylene hydride species and investigate their ability for CO_2 activation.

In 2010, we introduced the 2-iminocyclohexylidenebenzylamine ligand $L^{Cy}H$ (L^{Cy} = cyclo-C_6H_8-1-NAr-2-C(Ph)NAr, Ar = 2,6-$iPr_2C_6H_3$) for stabilising a germylene complex, and studied its reactivity towards water and ammonia.[12] Since the successful application of this ligand, we wanted to apply it also as a supporting ligand for the corresponding germylene hydride and the potentially isolable corresponding formate complexes. Herein, we report the use of this ligand ($L^{Cy}H$) for the synthesis of a new germylene hydride derivative and its application in hydrogenation of CO_2 to the germylene formate $L^{Cy}GeOCH(=O)$ (**2**). Complex **2** and the reported LGeOCH(=O) (**2′**) react readily with alane ($AlH_3{\cdot}NMe_3$) to afford deuterated methanol (CH_3OD) upon hydrolysis with D_2O. The trapping and full elucidation of key intermediates in the conversion of **2′** to methanol are also reported and shed light on the mechanism of CO_2 reduction mediated by germylene hydrides.

Results and discussion

Accordingly, the synthesis of the $L^{Cy}H$ stabilised germylene hydride complex was first investigated. Akin to the preparation of LGeH,[8] $L^{Cy}GeCl$ was treated with one molar equivalent of

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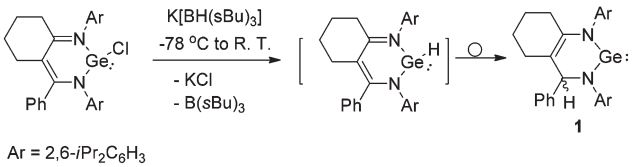


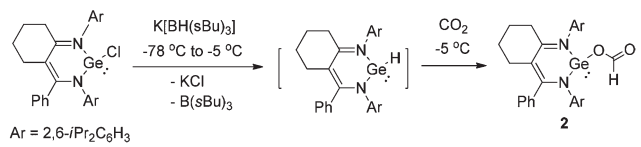
Scheme 1 Synthesis of compound **1** *via* Ge(II) hydride.

K[BH(*s*Bu)$_3$] in toluene at −78 °C and allowed to warm to room temperature. Unexpectedly, after a reaction time of 12 hours at ambient temperature, the expected germylene hydride complex (L^{Cy}GeH) was not isolated. Instead, L^{Cy}(H)Ge (**1**) was isolated as a single product with 84% yield (Scheme 1).

However, when the reaction process was monitored by ^{1}H NMR spectroscopy, after the mixture was stirred for 3 hours at room temperature, the characteristic resonance signal for Ge–H proton could indeed be observed at δ = 7.96 ppm which is comparable to that of LGeH (δ = 8.08 ppm).[11a] This indicates that L^{Cy}GeH is formed during the reaction, but it is labile and ultimately undergoes a 1,3-hydrogen transfer from the germanium centre to the backbone of the ligand to give the germylene **1** with a hydrogenated ligand scaffold as the thermodynamic product. A similar reaction mode was reported by Jones *et al.* when they attempted to use $^{t\mathrm{Bu}}$NacnacH ($^{t\mathrm{Bu}}$Nacnac = CH(*t*BuCNAr)$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) and $^{t\mathrm{Bu}}$MesNacnacH ligands ($^{t\mathrm{Bu}}$MesNacnac = CH(*t*BuCNMes)$_2$, Mes = 2,4,6-Me$_3$C$_6$H$_3$) to stabilise a germylene hydride. In both cases the only isolated products are diamido germylene complexes with 1,3-hydride migration to the backbone of the ligands.[11b,13] However, compound **1** cannot activate CO_2 even at elevated temperatures in toluene or benzene.

Although L^{Cy}GeH is only a kinetic product, we reasoned that it could be employed for hydrogenation of CO_2 to afford the germylene formate complex L^{Cy}GeOCH(=O) (**2**). Following this idea, L^{Cy}GeCl was reacted with K[BH(*s*Bu)$_3$] in toluene at −5 °C for 12 hours under a N_2 atmosphere, and then the gas atmosphere was changed with CO_2 through a freeze–pump–thaw cycle, and the reaction mixture was further stirred for five hours. From the reaction mixture, the germylene formate L^{Cy}GeOCH(=O) (**2**) could indeed be isolated in 77% yield (Scheme 2).

Both compounds **1** and **2** are yellowish solids, and are thermally robust (M.p. 178 °C (**1**); 165 °C (**2**)) without any decomposition when stored under a N_2 atmosphere at room temperature for several months. They are soluble in toluene, benzene and THF, and slightly soluble in *n*-hexane. They were fully characterised by NMR spectroscopy (^{1}H, ^{13}C), mass spectrometry, elemental analyses as well as single crystal X-ray



Scheme 2 Synthesis of compound **2**.

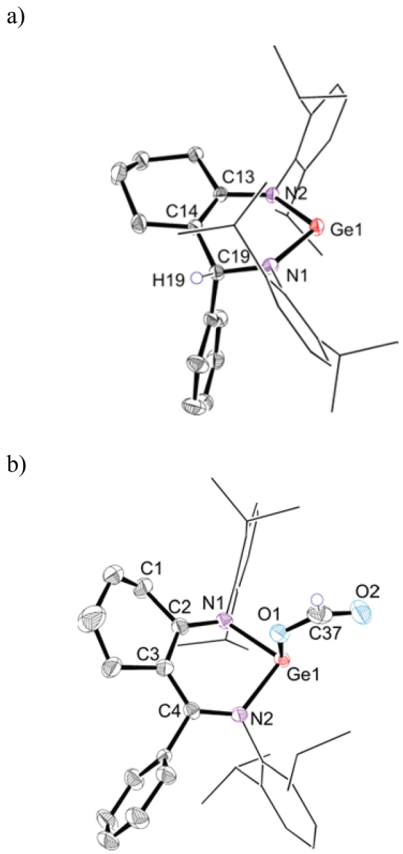


Fig. 1 Molecular structures of compounds **1** (a) and **2** (b) in the solid state. Thermal ellipsoids are drawn at the 50% probability level; the Dipp groups are depicted in wireframe style. Disorders at C36 and C38 of compound **2** and hydrogen atoms (except those at C19 of compound **1** and C37 of compound **2**) are omitted for clarity.

diffraction analyses. The resonance signal for the γ-H proton (PhC*H*NAr) in complex **1** is observed at δ = 4.75 ppm as a singlet in the ^{1}H NMR spectrum in C_6D_6 at room temperature. The corresponding carbon nucleus resonates at δ = 74.8 ppm in the ^{13}C{^{1}H} NMR spectrum. In the APCI-HR-MS spectrum, the signal for the molecular ion peak of **1** is found at *m*/*z* 595.3082 (calcd: *m*/*z* 595.3102), whereas the molecular ion peak for compound **2** is not found, but the signal for the molecule fragment corresponding to loss of the formate group is observed at *m*/*z* 593.2936 (calcd: *m*/*z* 593.2946). The resonance signal for the proton at the formate group in **2** is shown at δ = 8.78 ppm in the ^{1}H NMR spectrum, which is comparable to that of the formate group in **2′** (δ = 8.4 ppm); the corresponding ^{13}C signal is revealed at δ = 164.4 ppm in the ^{13}C NMR spectrum. The molecular structures of complexes **1** and **2** are shown in Fig. 1.

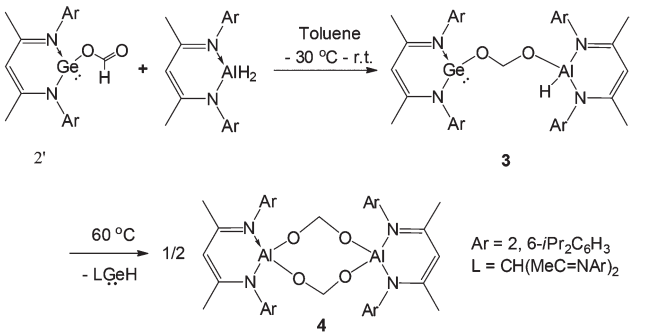
Complex **1** crystallises in the triclinic space group *P*1, which is a chiral crystal system. The germanium centre is coordinated by the N1 and N2 atoms. The distances of Ge1 to N1 and N2 are 1.8250(19) Å and 1.867(2) Å, respectively. They are comparable to those in $L^{Cy'}$Ge ($L^{Cy'}$ = cyclo-C$_6$H$_7$-1-NAr-2-C(Ph)NAr, Ar = 2,6-iPr$_2$C$_6$H$_3$) which bears a dianionic ligand (1.861 and 1.843 Å).[12] The bond distances of C14–C19 (1.513 (3) Å) and

C13–C14 (1.346(3) Å) indicate the single and double bond character, respectively. This is in accordance with the structure portrayed for **1** in Scheme 1. Compound **2** crystallises in the monoclinic space group *P*2/*c* and the germanium centre features a trigonal pyramidal geometry. The Ge1 centre deviates from the plane defined by N1–C2–C3–C4–N2 by 0.534 Å. The distances of Ge1–N1, Ge1–N2 (1.976(2) and 1.988(2) Å) and Ge1–O1 (1.958(2) Å) are consistent with those observed in **2′** (Ge–N: 1.969(2) and 1.968(2) Å, Ge–O: 1.9339(18) Å).[8]

Roesky *et al.* demonstrated that the germylene formate **2′** could be converted to formic acid and methanol with $LiNH_2{\cdot}BH_3$ and $NH_3{\cdot}BH_3$ as the hydride sources upon workup with water, respectively.[9] Very recently, Sakaki *et al.* showed that LGeH can act as a catalyst in CO_2 hydrogenation when a suitable silane is applied as the hydride source based on a theoretical study.[10] Inspired by these results, we were interested in introducing alane as a hydride transfer source for CO_2 hydrogenation and elucidating the mechanism of the reaction.

We chose $Me_3N{\cdot}AlH_3$ as the hydride source and used it to react with 1/3 molar equivalent of **2′** and compound **2**, respectively. The ^{1}H NMR spectra in C_6D_6 showed that both the reactions proceeded smoothly to give the corresponding germylene hydride complexes in almost quantitatively yields within one hour at room temperature (Fig. 2 and ESI†).[14] After stirring for two hours in toluene, the reactions were quenched with D_2O at 0 °C. The yields of CH_3OD were determined as 46% (**2′**) and 42% (**2**) by ^{1}H NMR spectroscopy with 1,4-dioxane as an internal standard.

After obtaining these results, we proceeded to elucidate the stepwise process of this reaction. For this purpose, $LAlH_2$ (L = $CH(MeC{=}NAr_2)_2$, Ar = 2,6-$iPr_2C_6H_3$)[15] was applied as a milder hydride delivery agent to react with **2′**. By the reaction of **2′** with one molar equivalent of $LAlH_2$, the carbonyl group is further hydrogenated to afford the striking compound **3** as an OCH_2O bridged heterobimetallic complex (Scheme 3). The resonance signal for the protons at the OCH_2O group is observed at δ = 4.48 ppm, the γ-H protons of the β-diketiminato ligands resonate at δ = 4.90 and 5.02 ppm, respectively, and their integrate ratio is 2 : 1 : 1, which is in accordance with the structure depicted for compound **3**. Hence, the hydrogenation of the formate group to the OCH_2O group represents the second step for CO_2 hydrogenation. While there is still one Al–H in compound **3**, the yellow solution of **3** in THF gradually turned to red at room temperature, and so we tested the thermal stability of **3**. From a ^{1}H NMR spectroscopic investigation, compound **3** was decomposed to give LGeH and compound **4** after heating at 60 °C for 3 hours in THF (Scheme 3). From the reaction mixture, compound **4** was isolated as a colorless crystalline product in 60% yield. The proton signals for the OCH_2O group and the γ-H proton in the β-diketiminate ligand are observed at δ = 4.74 and 5.00 ppm, respectively, with the integrate ratio of 4 : 2. In this step, the LGeH is regenerated. Moreover, we tried to cleave the O–CH_2O bond in **4** with various hydride sources, but all attempts failed, probably due to the steric crowding resulting from the bulky β-diketiminato ligand.



Scheme 3 Syntheses of compounds **3** and **4**.

The molecular structures of compounds **3** and **4** are shown in Fig. 3 and 4. Complexes **3** and **4** crystallise in the monoclinic space group *C*2/*c*. The Ge1 has a trigonal pyramidal geometry and Al1 feature a tetrahedral coordination in **3**, and they are bridged by the OCH_2O group. The Ge1–O1 bond length (1.854(4) Å) is shorter than that in the starting material **2′** (1.9339(18) Å),[8] whereas it is comparable to that in LGeOiPr

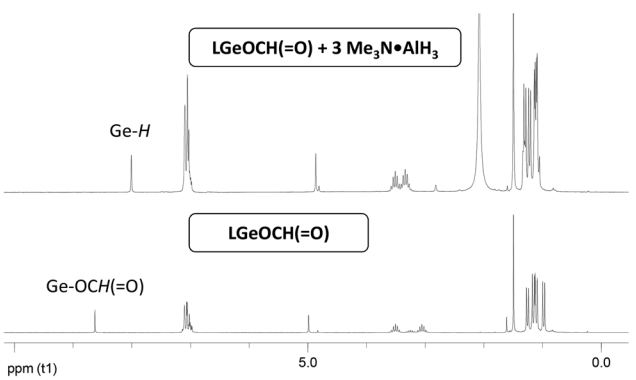


Fig. 2 ^{1}H NMR spectra of the reaction of **2′** with 3 molar equivalents of $NMe_3{\cdot}AlH_3$ for 60 min (top) and **2′** in C_6D_6 (bottom).

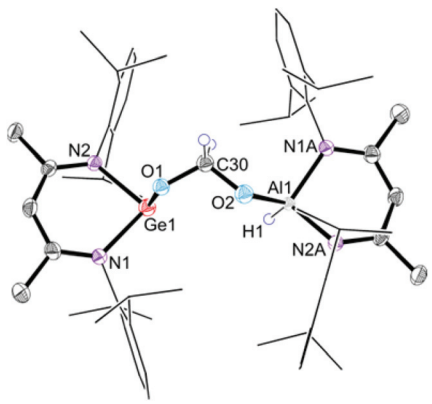


Fig. 3 Molecular structure of compound **3** in the solid state. Thermal ellipsoids are drawn at the 50% probability level; the Dipp groups are depicted in wireframe style. Disorders at the core part $GeOCH_2OAl$ of compound **3** and hydrogen atoms (except those at C30 and Al1) are omitted for clarity. Operation symmetry for all atoms labelled with "A": $-x + 1/2, -y + 1/2, -z + 2$ (**3**).

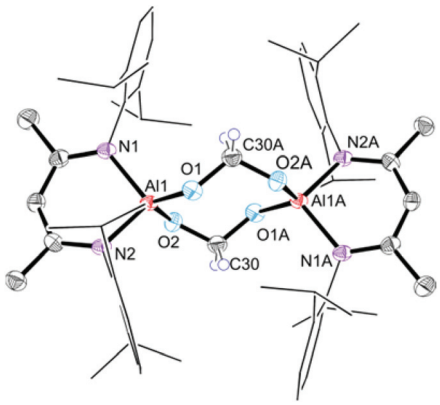
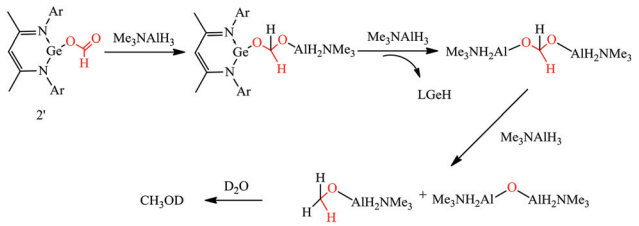


Fig. 4 Molecular structure of compound **4** in the solid state. Thermal ellipsoids are drawn at the 50% probability level; the Dipp groups are depicted in wireframe style. Hydrogen atoms (except those at C30 and C30A) are omitted for clarity. Operation symmetry for all atoms labelled with "A": $-x + 1/2, -y + 1/2, -z + 1$ (**4**).



Scheme 4 Plausible reaction mechanism for germylene mediated CO_2 reduction to CH_3OD with alane.

(1.821(2) Å).[16] The Al1–O2 bond distance (1.807(3) Å) is akin to those in $[\{LAlMe(\mu\text{-}O)AlMe_2\}]_2$ (av. 1.8493 Å).[17] Compound **4** is a binuclear aluminium complex with a $(AlOCH_2O)_2$ core structure. The Al–N (1.8979(13) and 1.8963(13) Å) and Al–O (1.7123(11) and 1.7239(11) Å) bond lengths are similar to those in $LAl[OB(3\text{-}MeC_6H_4)]_2(\mu\text{-}O)$ (Al–N: 1.872(2) and 1.862(2) Å; Al–O: 1.7362(17) and 1.7418(17) Å).[18]

Based on the model reaction of $LAlH_2$ with **2′** and the isolation of complexes **3** and **4**, the stepwise process of the conversion of **2** or **2′** with $Me_3N{\cdot}AlH_3$ to methanol upon hydrolysis with water could be explained as follows (Scheme 4): complex **2′** is hydrogenated to form the adduct $LGeOCH_2OAlH_2{\cdot}NMe_3$, and the subsequent Al–H hydride of $Me_3N{\cdot}AlH_3$ transfer to the Ge centre regenerates LGeH. Concomitantly, $Me_3N{\cdot}AlH_2O\text{-}CH_2OAlH_2{\cdot}NMe_3$ is formed which is continuously converted to $Me_3N{\cdot}AlH_2$–OMe and $Me_3N{\cdot}AlH_2OH_2Al{\cdot}NMe_3$ with O–CH_2O bond cleavage. Hydrolysis of $Me_3N{\cdot}AlH_2$–OMe with D_2O then yields CH_3OD as a C1 product.

Conclusion

In conclusion, we demonstrated that the novel formate compound $L^{Cy}GeOCH(=O)$ (**2**) and the previously reported $LGeOCH(=O)$ (**2′**) can both be efficiently hydrogenated to yield methanol using alane as the hydride source upon workup with water. The germylene hydrides are concomitantly regenerated in this process. Based on the reaction of the mild hydrogen delivery agent ($LAlH_2$) with $LGeOCH(=O)$ (**2′**) as a model reaction, we suggested a plausible mechanism for the formation of methanol with the isolation of $LGeOCH_2OAl(H)L$ (**3**) and $(LAlOCH_2O)_2$ (**4**), respectively. These studies shed new light on the reduction of CO_2 mediated by germylene hydrides.

Experimental section

All experiments were carried out under dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled and degassed prior to use. The NMR spectra were recorded on Bruker spectrometers (AV400 or AV200) referenced to residual solvent signals as internal standards (^1H NMR: $CDCl_3$, 7.26 ppm; C_6D_6, 7.16 ppm; and $^{13}C\{H\}$ NMR: $CDCl_3$, 77.0 ppm; C_6D_6, 128.1 ppm) or with an external standard. Concentrated solutions of samples in C_6D_6 or $CDCl_3$ were sealed off in a Young-type NMR tube for measurements. Melting points were recorded on a "Melting point tester" device from BSGT Company and are uncorrected. All the samples were sealed off in capillary under vacuum and each sample was measured in duplicate. High resolution mass spectra (APCI, atmosphere pressure chemical ionization) were recorded on an Orbitrap LTQ XL of a Thermo Scientific mass spectrometer and the raw data were evaluated using the Xcalibur computer program. For the single crystal X-ray structure analyses the crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data of compounds **1** and **2** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo-Kα radiation, λ = 0.71073 Å), and the data of compounds **3** and **4** were collected on an Oxford Diffraction Supernova, Single source at offset, Atlas at 150 K (Cu-Kα radiation, λ = 1.5418 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97[19] software package. The positions of the H atoms were calculated and considered isotropically according to a riding model.

Commercially available reagents were purchased from Aldrich, Acros and used as received. $L^{Cy}H$, $L^{Cy}GeCl$ (L^{Cy} = cyclo-C_6H_8-1-NAr-2-C(Ph)NAr, Ar = 2,6-i$Pr_2C_6H_3$),[12] $LGeOCH(=O)$ (**2′**)[8] and $LAlH_2$[15] (L = CH[C(Me)NAr]$_2$, Ar = 2,6-i$Pr_2C_6H_3$) were synthesized according to published procedures.

Compound $L^{Cy}(H)Ge$ (1)

$L^{Cy}GeCl$ (0.628 g, 1 mmol) was placed in a Schlenk flask (100 mL) in the glovebox. Toluene (30 mL) was transferred into the flask *via* cannula under stirring at room temperature and a clear yellow solution was formed. The solution was cooled to −78 °C, and $K[BH(sBu)_3]$ (1 mL, 1 mmol, 1 M solution in THF) was added dropwise to the solution *via* a syringe. The mixture was allowed to warm to room temperature and stirred for another 12 hours. The obtained red solution was concentrated to 10 mL and filtered. The filtrate was left at 0 °C for 24 hours to afford a yellow crystalline product (**1**). The product was

collected by decantation of the supernatant and the obtained solid was dried *in vacuo* for several hours. Yield: 0.50 g (0.84 mmol, 84%). M.p. 178 °C (dec.). ^{1}H NMR (200.1 MHz, C_6D_6, 298 K): δ = 0.53 (d, 3 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.10 (d, 3 H, $^3J_{H-H}$ = 7.0 Hz, CH(CH_3)$_2$), 1.25 (d, 3 H, $^3J_{H-H}$ = 6.6 Hz, CH(CH_3)$_2$), 1.28 (d, 9 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.37–1.44 (m, 7 H, Cy-CH_2 (4 H) + CH(CH_3)$_2$ (3 H)), 1.47 (d, 3 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.75–2.01 (m, 4 H, Cy-CH_2), 3.13 (sept, 1 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 3.55 (sept, 1 H, $^3J_{H-H}$ = 6.8 Hz, CH-(CH$_3$)$_2$), 3.91 (sept, 2 H, $^3J_{H-H}$ = 7.0 Hz, CH(CH$_3$)$_2$), 4.75 (s, 1 H, γ-*H* (PhC*H*NAr)), 7.04–7.41 (m, 11 H, Ar-*H* and Ph-*H*). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 298 K): δ = 22.5, 22.9 (iPr-*C*H$_3$), 23.0 (Cy-*C*H$_2$), 23.5(iPr-*C*H$_3$), 23.7 (Cy-*C*H$_2$), 23.8 (iPr-*C*H$_3$), 25.2, 26.1, 26.2, 26.9 (iPr-*C*H), 27.9 (Cy-*C*H$_2$), 28.1, 28.2, 28.3, 28.4 (iPr-*C*H$_3$), 29.9 (Cy-*C*H$_2$), 74.8 (γ-*C*), 109.1 (CH$_2$*C*CNAr), 123.2, 123.8, 124.0, 124.2, 126.4, 127.0, 127.1, 128.2, 128.3 (Ar-*C*H), 134.4, 140.3, 143.7, 145.0, 146.9, 147.1, 147.2, 148.1 (Ar-*C* and CH$_2$C*C*NAr). Elemental analysis for $C_{37}H_{48}GeN_2$: calcd: C, 74.89; N, 4.72; H, 8.15; found: C, 74.19; N, 4.48; H, 8.30. APCI-HR-MS: calcd for [$C_{37}H_{49}GeN_2$ (M + H)]$^+$: *m*/*z* 595.3102; found: *m*/*z* 595.3082.

Compound L^{Cy}GeOCH(=O) (2)

L^{Cy}GeCl (1.26 g, 2 mmol) was placed in a Schlenk flask (100 mL) in the glovebox. Toluene (30 mL) was transferred into the flask *via* cannula under stirring at room temperature and a clear yellow solution was formed. The solution was cooled to −78 °C, and K[BH(*s*Bu)$_3$] (2 mL, 2 mmol, 1 M solution in THF) was added dropwise to the solution *via* a syringe. The mixture was then placed in a cooled water–salt bath (*ca.* −5 °C), and allowed to stir at this temperature for 12 hours. Then the atmosphere was changed to CO_2 by a freeze–pump–thaw cycle, and the mixture was stirred under a CO_2 atmosphere for 12 hours. All the volatiles were removed *in vacuo* and the residue was washed with hot (*ca.* 50 °C) *n*-hexane (20 mL), and the solution was filtrated. The remaining residue is the pure product (**2**) on the basis of ^{1}H NMR spectroscopy. The filtrate was left at room temperature for 12 hours to yield crystals of **2**, which are suitable for X-ray single crystal diffraction analysis. Total yield: 1.01 g (1.55 mmol, 77%). M.p. 165 °C (dec.). ^{1}H NMR (200.1 MHz, C_6D_6, 298 K): δ = 0.91 (d, 3 H, $^3J_{H-H}$ = 6.6 Hz, CH(CH_3)$_2$), 1.02 (d, 3 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.12–1.23 (m, 16 H, Cy-*H* (4 H) + CH(CH_3)$_2$ (12 H)), 1.27 (d, 3 H, $^3J_{H-H}$ = 6.6 Hz, CH(CH_3)$_2$), 1.33 (d, 3 H, $^3J_{H-H}$ = 6.6 Hz, CH(CH_3)$_2$), 1.86–2.21 (m, 4 H, Cy-*H*), 3.03–3.31 (m, 2 H, CH(CH$_3$)$_2$), 3.44–3.72 (m, 2 H, CH(CH$_3$)$_2$), 6.67–6.92 (m, 7 H, Ar-*H* and Ph-*H*), 7.03–7.22 (m, 4 H, Ar-*H* and Ph-*H*), 8.78 (s, 1 H, –OC*H*(=O)). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 298 K): δ = 21.0 (Cy-*C*H$_2$), 22.3(Cy-*C*H$_2$), 22.9, 23.3, 24.2, 24.3, 24.4, 26.8 (iPr-*C*H$_3$), 27.2, 27.6 (iPr-*C*H), 27.9 (iPr-*C*H$_3$), 28.6, 28.7(iPr-*C*H), 28.8 (Cy-*C*H$_2$), 28.9(iPr-*C*H$_3$), 31.1(Cy-*C*H$_2$), 107.0 (γ-*C*), 123.2, 124.2, 125.3, 126.9, 127.0, 127.5, 127.7, 127.8, 127.9, 128.0, 128.6 (Ar-*C*H), 137.9, 139.9, 140.4, 143.0, 145.1, 146.0, 146.7 (Ar-*C*), 164.4 (–O*C*H(=O)), 165.8 (Cy-*C*N), 168.7 (Ph-*C*N). Elemental analysis for $C_{38}H_{48}GeN_2O_2$ (%): calcd: C, 71.60; N, 4.39; H, 7.59; found: C, 71.56; N, 4.37; H, 7.93.APCI-HR-MS: calcd for [$C_{37}H_{47}GeN_2$ (M − CO_2H)]$^+$: *m*/*z* 593.2946; found: *m*/*z* 593.2936. IR (KBr): ν = 2870 (O*C*(=O)–*H*), 1657(O*C*(=*O*)–H) cm^{-1}.

Compound LGeOCH$_2$OAl(H)L (3)

LGeOCH(=O) (**2′**) (0.268 g, 0.5 mmol) and LAlH$_2$ (0.224 g, 0.5 mmol) were placed in a Schlenk flask (100 mL) in the glovebox. Toluene (30 mL) was transferred to the mixture *via* cannula under stirring at −50 °C. The solution was allowed to warm to room temperature and stirred for another 12 hours to give a clear yellow solution. The solution was concentrated to *ca.* 5 mL and filtrated. The obtained filtrate was left at 0 °C for 24 hours to give yellow crystals of compound **3**. The product was collected by decantation of the supernatant and dried *in vacuo* for several hours. Yield: 0.36 g (0.37 mmol, 74%). M.p. 96 °C (dec.). ^{1}H NMR (400.2 MHz, $CDCl_3$, 298 K): δ = 0.62 (d, 6 H, $^3J_{H-H}$ = 6.4 Hz, CH(CH_3)$_2$), 0.79 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 0.94 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.01 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.02 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.07 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.15 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.21 (d, 6 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.62 (s, 6 H, α-CH_3), 1.67 (s, 6 H, α-CH_3), 2.98–3.12 (m, 6 H, CH(CH$_3$)$_2$), 3.17 (sept, 2 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 4.48 (s, 2 H, OCH_2O), 4.90 (s, 1 H, γ-H), 5.02 (s, 1 H, γ-H), 6.84–6.86 (m, 2 H, Ar-*H*), 6.98–7.03 (m, 2 H, Ar-*H*), 7.06–7.26 (m, 8 H, Ar-*H*). The resonance signal for Al-*H* is not observed in the spectrum. ^{13}C{^{1}H} NMR (100.1 Hz, $CDCl_3$, 298 K): δ = 23.1 (α-*C*H$_3$), 23.4(α-*C*H$_3$), 24.1, 24.2, 24.6, 24.7, 25.1, 25.8 (iPr-*C*H$_3$), 27.3, 27.7, 28.0, 28.7 (iPr-*C*H), 85.9 (O*C*H$_2$O), 96.2 (γ-*C*), 96.4 (γ-*C*), 123.3, 123.9, 124.1, 124.8, 126.3, 126.7, 126.8, 128.2, 129.0 (Ar-*C*H), 139.4, 140.7, 143.1, 143.8, 143.9, 146.0 (Ar-*C*), 163.2 (*C*NAr), 169.9 (*C*NAr). Elemental analysis for $C_{59}H_{85}AlGeN_4O_2$ (%): calcd: C, 72.17; N, 5.71; H, 8.72; found: C, 72.40; N, 5.86; H, 8.55. APCI-HR-MS: calcd for [$C_{59}H_{86}AlGeN_4O_2$ (M + H)]$^+$: *m*/*z* 983.5772; found: *m*/*z* 983.5751.

Compound LAl(OCH$_2$O)$_2$AlL (4)

Compound **3** (0.491 g, 0.5 mmol) was placed in a Schlenk flask (50 mL) in the glovebox. THF (10 mL) was transferred to the flask *via* cannula at room temperature. The yellow solution was heated at 60 °C for 12 hours under stirring, and an orange-red solution was formed. All volatiles were removed *in vacuo*. The residue was extracted firstly with *n*-hexane (10 mL) (to remove the LGeH), and then it was extracted with toluene (10 mL) to give a yellow filtrate. The toluene solution was concentrated to *ca.* 5 mL and filtrated. The filtrate was left at 0 °C for 24 hours to give colorless crystals of compound **4**. The product was collected by removing the mother liquor and dried under vacuum for several hours. The mother liquor was further concentrated to *ca.* 3 mL, and afforded another portion of product after crystallization at −30 °C. Total yield: 0.15 g (0.15 mmol, 60%). M.p. 191 °C. ^{1}H NMR (200.1 MHz, $CDCl_3$, 298 K): δ = 0.78 (d, 24 H, $^3J_{H-H}$ = 6.6 Hz, CH(CH_3)$_2$), 0.95 (d, 24 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$), 1.55 (s, 12 H, α-CH_3), 3.06 (sept, 8 H, $^3J_{H-H}$ = 6.8 Hz, CH(CH$_3$)$_2$), 4.74 (s, 4 H, OCH_2O), 5.00 (s, 2 H, γ-*H*), 6.96 (s, 3 H, Ar-*H*), 7.00 (s, 4 H, Ar-*H*), 7.14–7.21 (m, 5 H, Ar-*H*). ^{13}C{^{1}H}

NMR (50.3 Hz, $CDCl_3$, 298 K): δ = 23.5 (α-CH_3), 24.4(CH-(CH_3)$_2$), 24.7(CH(CH_3)$_2$), 27.9 (CH(CH_3)$_2$), 85.7 (OCH_2O), 97.1 (γ-*C*), 124.1, 126.8 (Ar-*C*H), 140.4, 144.2 (Ar-*C*), 170.3 (*C*NAr). Elemental analysis for $C_{60}H_{86}Al_2N_4O_4$ (%): calcd: C, 73.44; N, 5.71; H, 8.83; found: C, 73.72; N, 5.89; H, 8.65. APCI-HR-MS: calcd for $[C_{60}H_{87}Al_2N_4O_4$ (M + H)]$^+$: *m*/*z* 981.6353; found: *m*/*z* 981.6340.

Conversion of 2 and 2′ to CH_3OD with $Me_3N{\cdot}AlH_3$

The germylene–formate **2** or **2′** (0.25 mmol) and $Me_3N{\cdot}AlH_3$ (0.75 mmol) was placed in a Schlenk flask in the glovebox. Toluene (10 mL) was added to the flask *via* a syringe at room temperature under stirring. The mixture was allowed to stir for another two hours, and cooled to 0 °C, D_2O was added to the solution and stirred for 10 minutes. The formed solid was separated using a centrifuge, and a clear two phase was formed. The aqueous phase was collected and 1,4-dioxane was added to it as an internal standard to determine the yields of CH_3OD by ^{1}H NMR spectroscopy.[9] Yields of CH_3OD: 42% (**2**) and 46% (**2′**).

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